Quantifying anthropogenic influences on the atmospheric chemistry of the western Sierra Nevada:

A background to assessing the role of biogenics

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Collaborators

Hydrocarbon, ozone and meteorological observations
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Nitrogen Oxide observations and modeling
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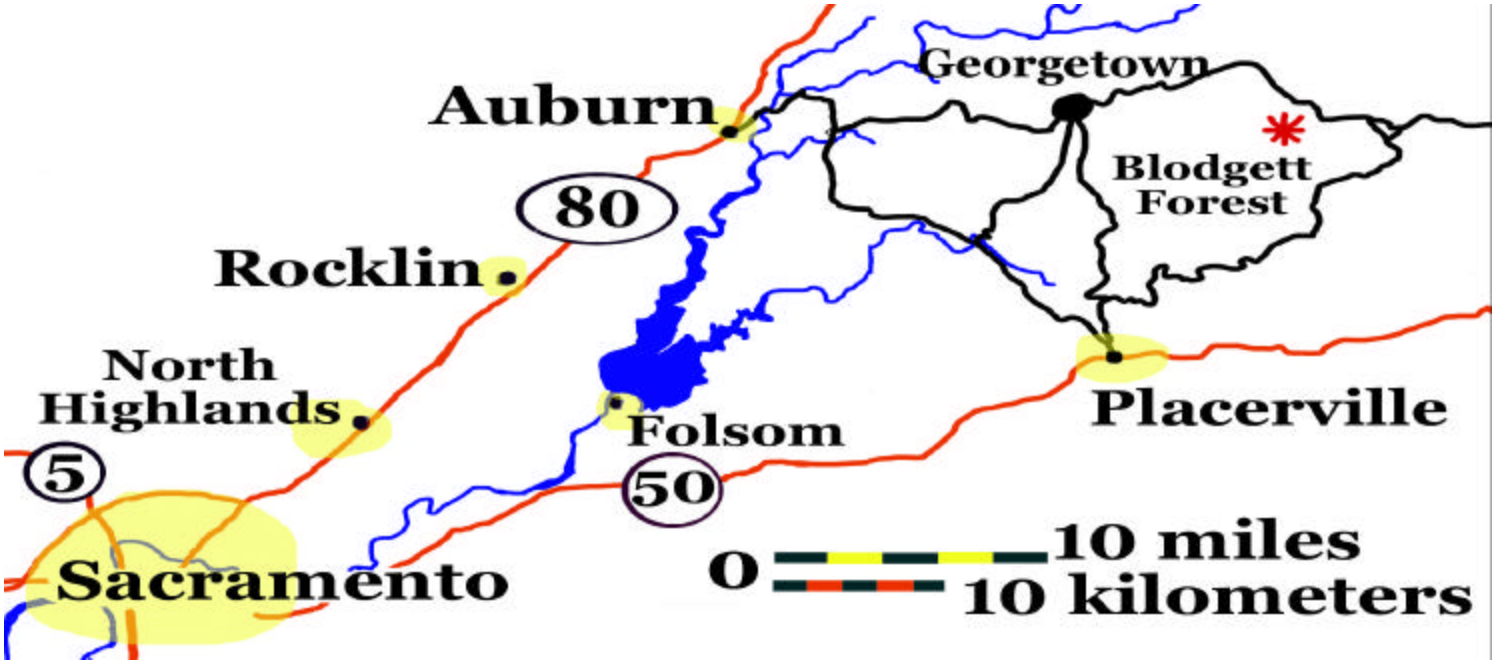
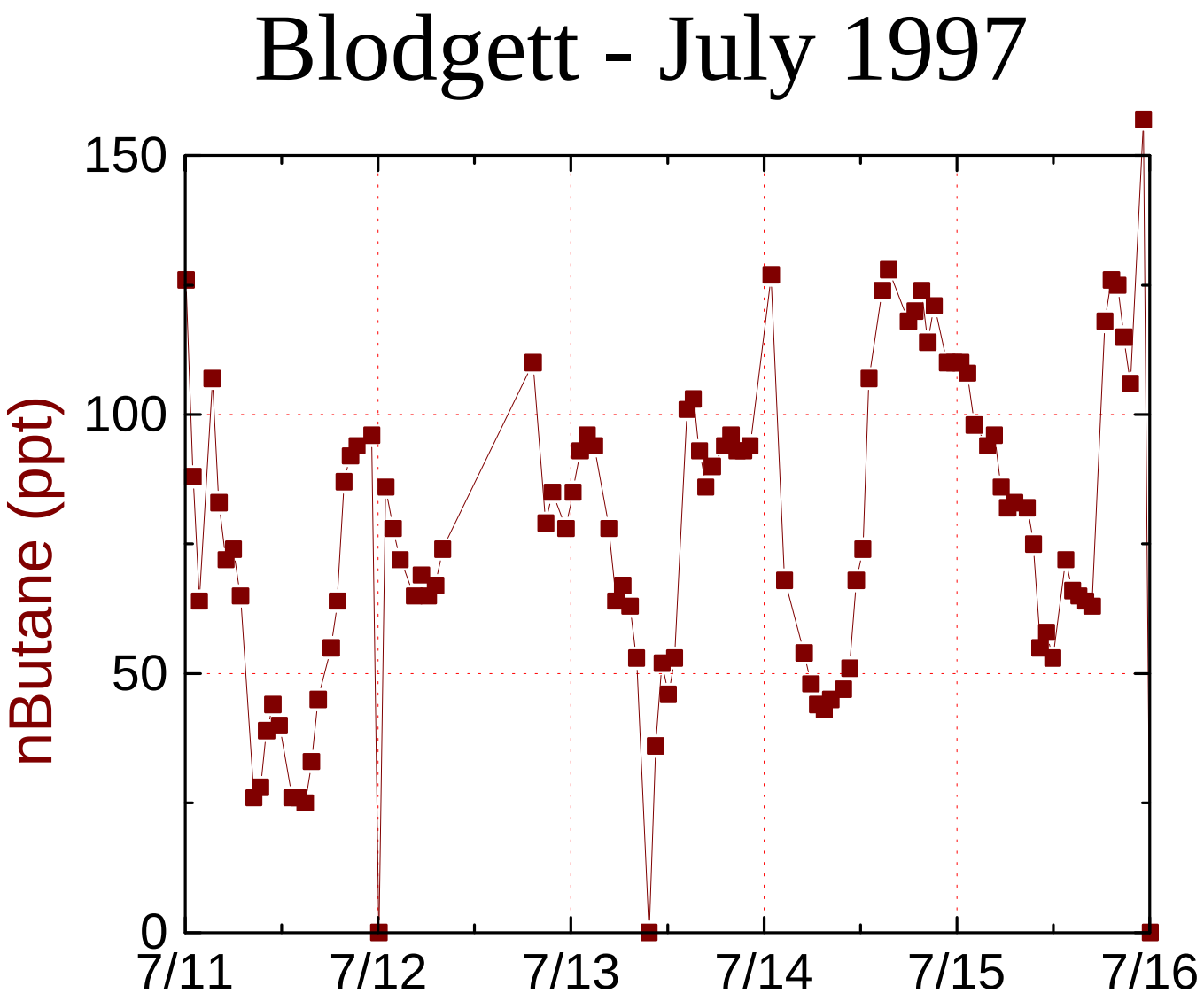
Cohen Group Research at Blodgett Forest

- Ozone Abundance and Chemistry
- NO_x and NO_y Photochemistry and Fluxes
- Connections across urban-regional-global scales

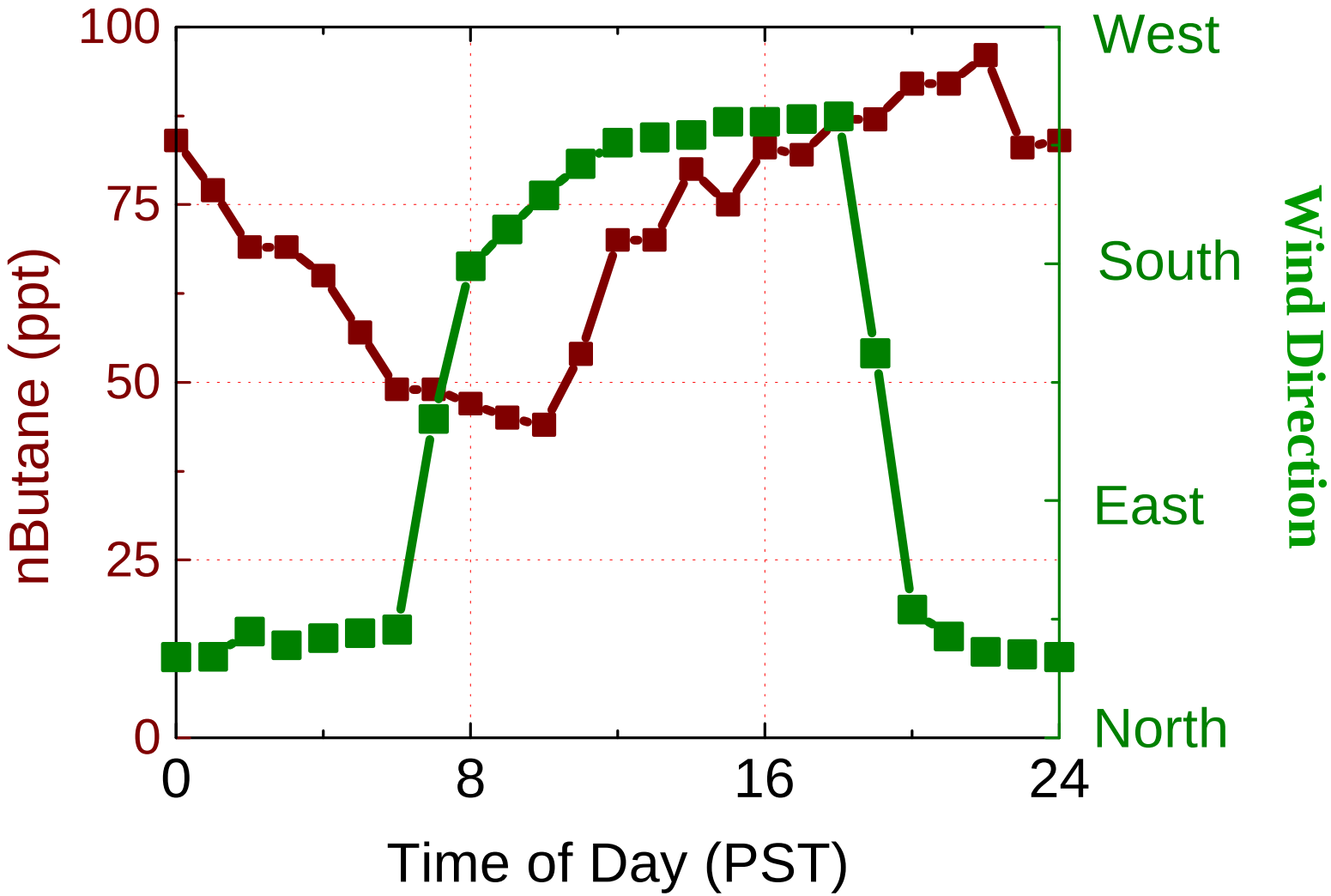


Hydrocarbon Measurements - 1997

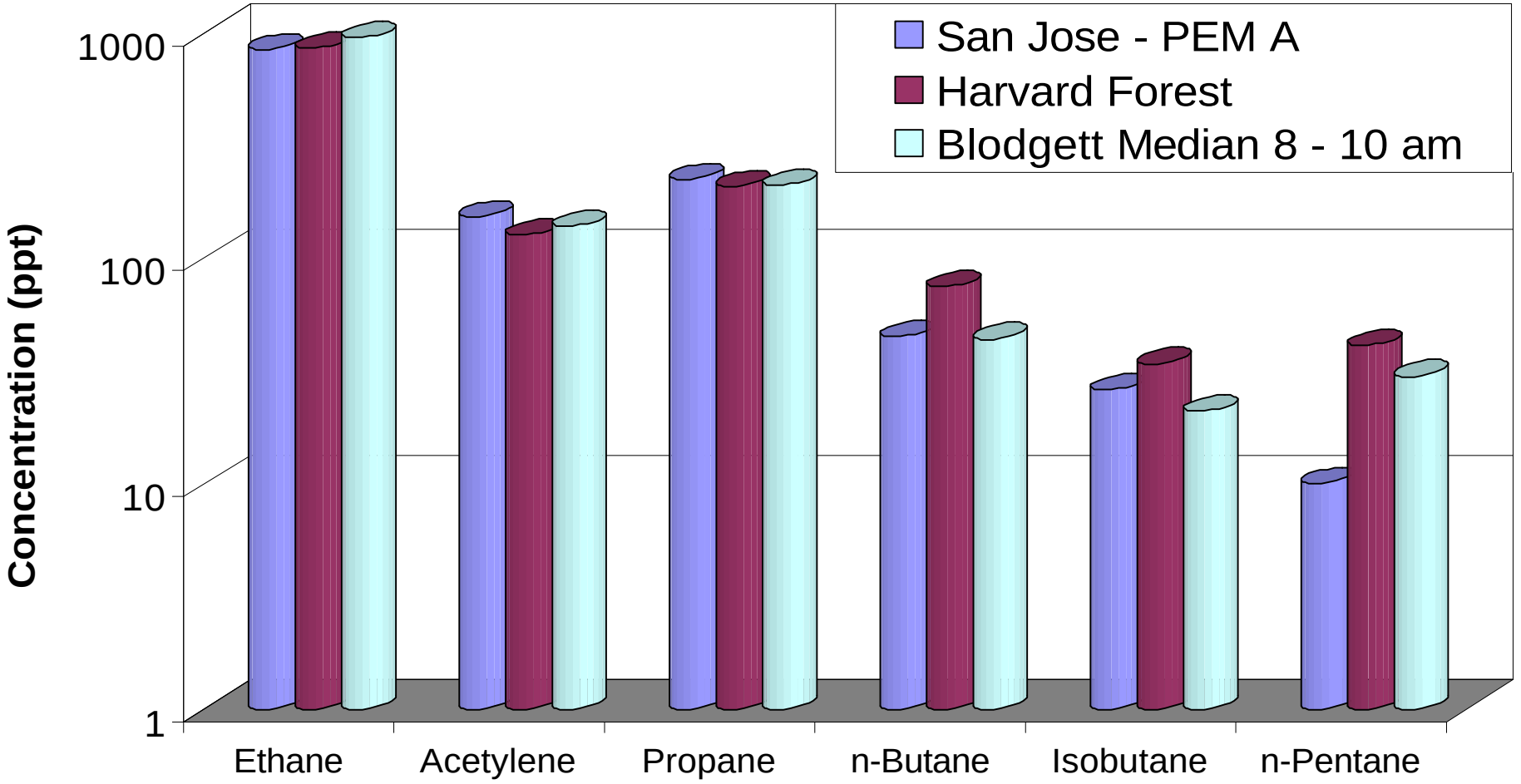
- Sampling from 6m above canopy
- Trapped on Carbon Black and Molecular Sieve at -80°C
- 20 minute averages on PLOT Rt-Alumina and DB-WAX columns
- Detection limit: 6-8 pptv
- Precision: 6%

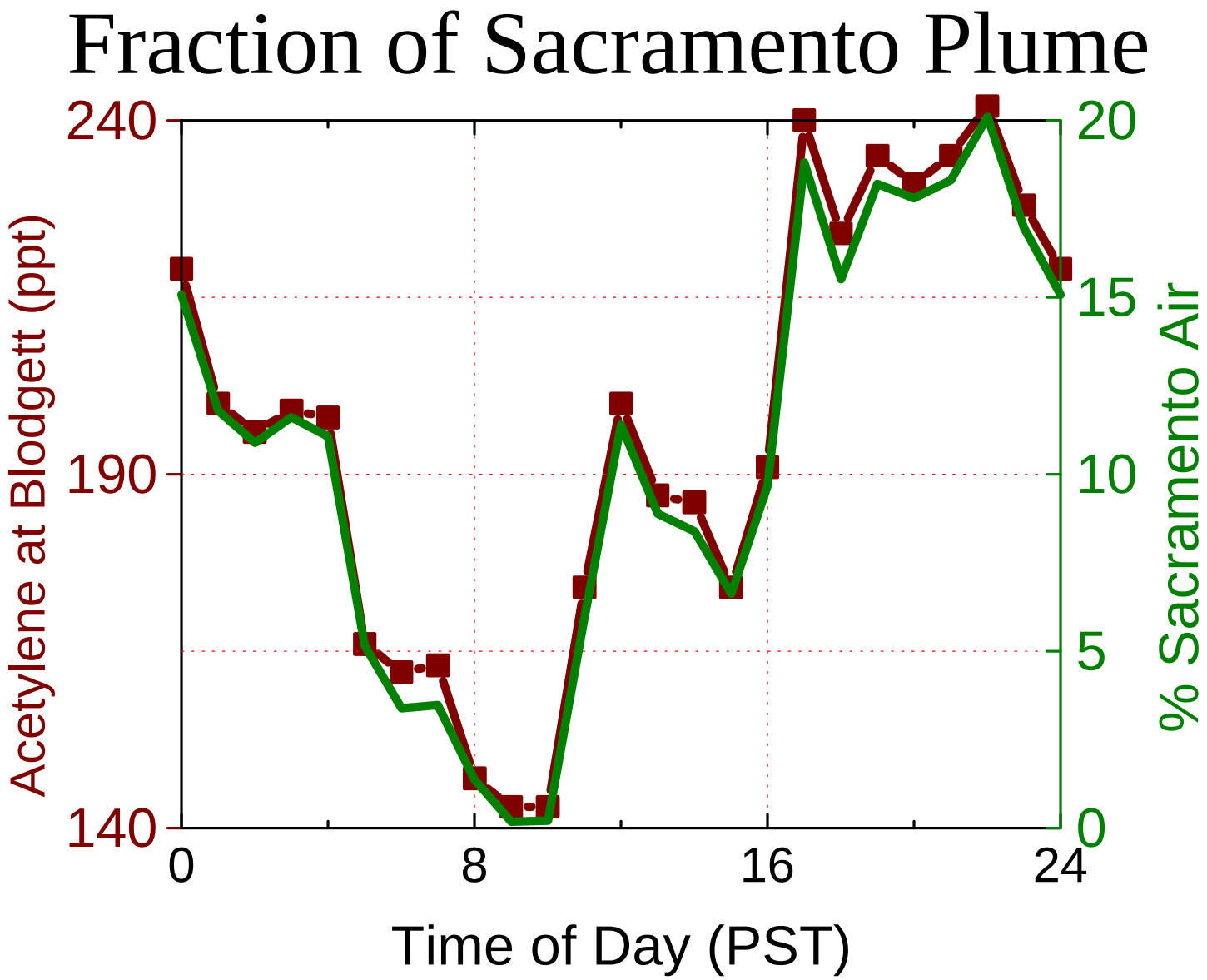

Blodgett - July 1997
nButane (ppt)
150
100
50
0
7/11
7/12
7/13
7/14
7/15
7/16

Blodgett - Diurnal Pattern

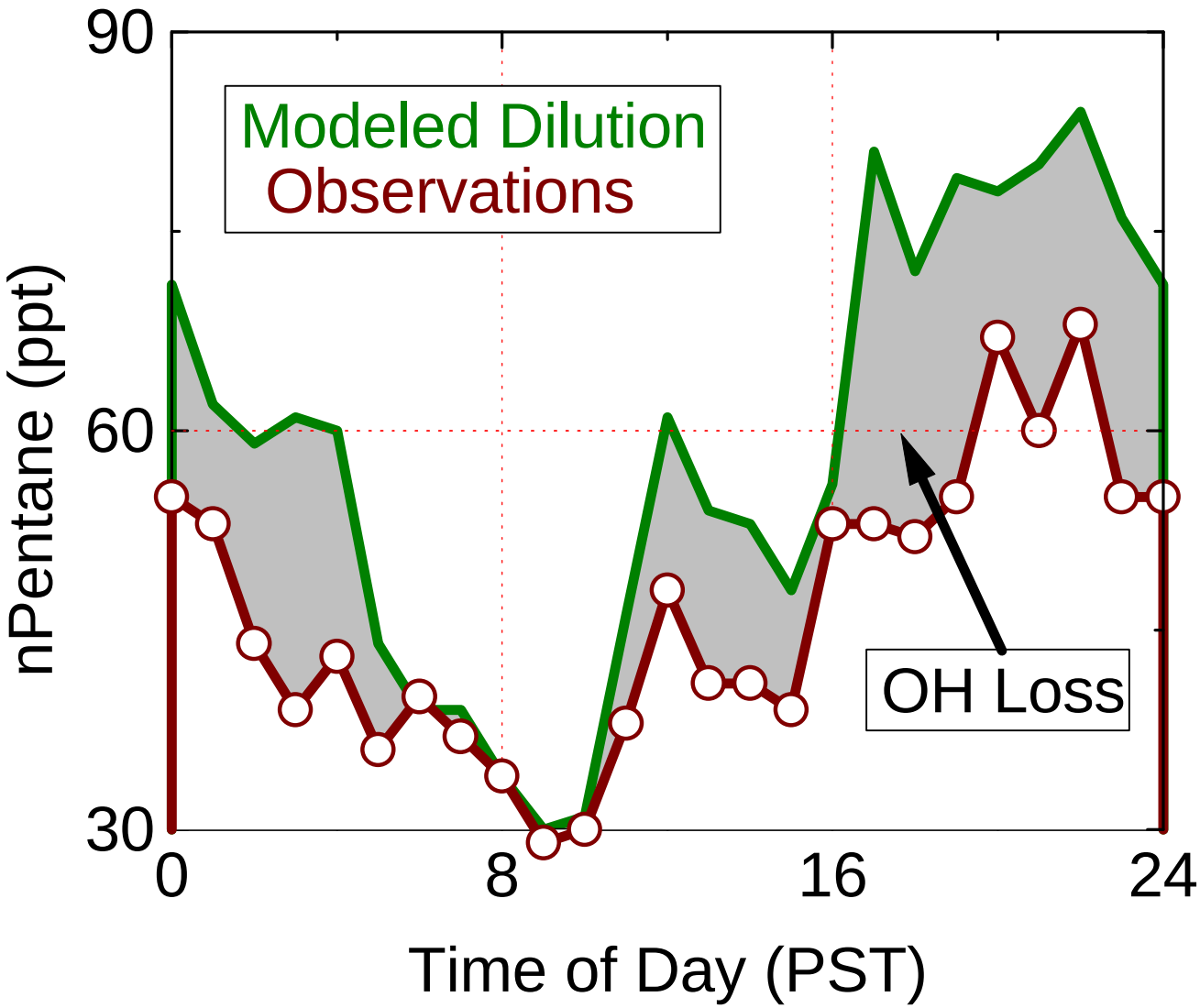


Air Observed at Blodgett in the Mornings is Clean Continental Background




Fraction of Sacramento Plume
240
190
140
Acetylene at Blodgett (ppt)
20
15
10
5
0
% Sacramento Air
0
8
16
24
Time of Day (PST)

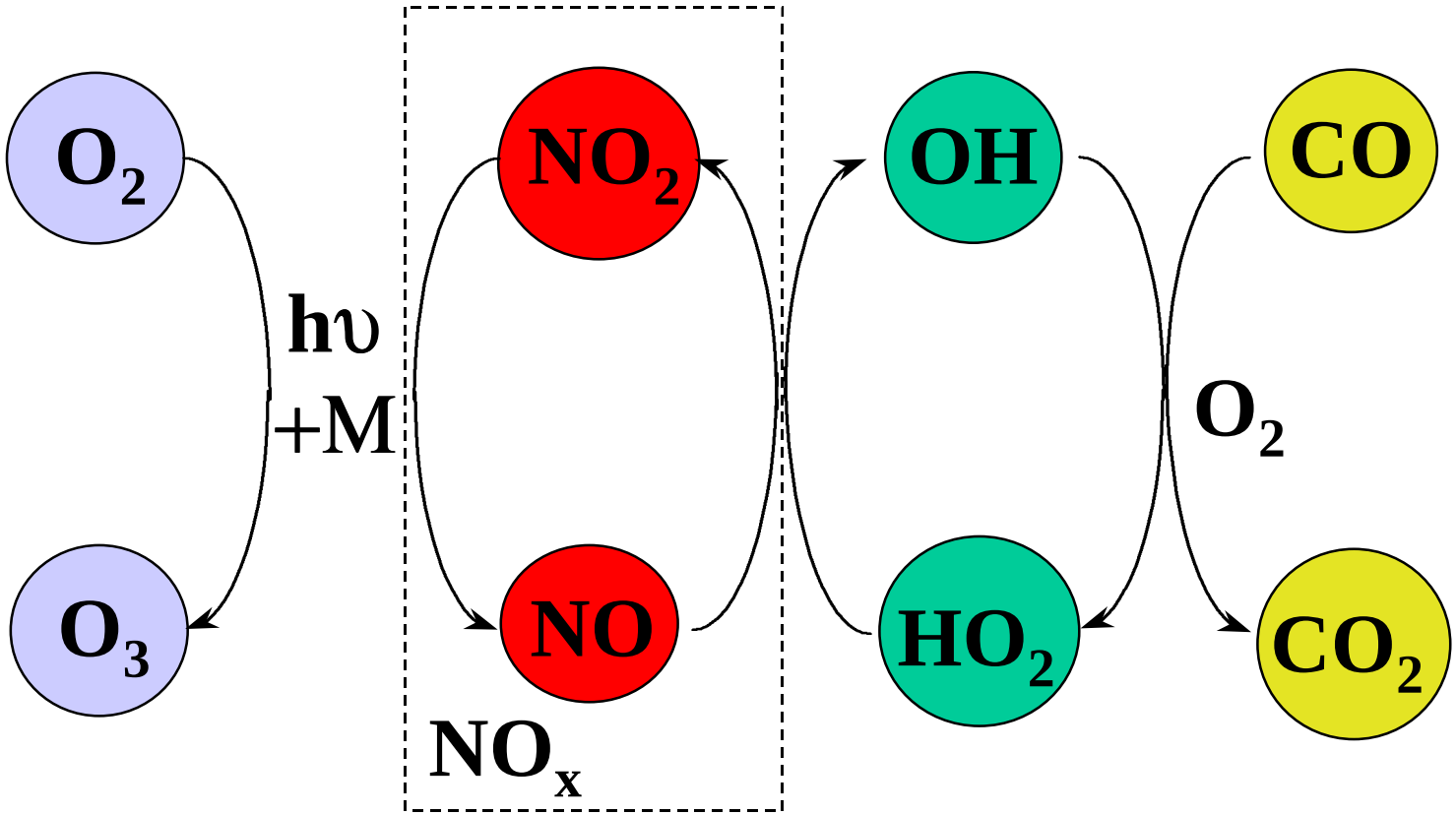
Loss by Reaction with OH



Summary

- Downslope flow brings extremely clean air masses to the foothills with continental background levels of anthropogenic hydrocarbons
- Upslope flow transports the expanding and diffusing Sacramento plume. By the time it gets to Blodgett, this plume is a mixture of 20% Sacramento air and 80% background air.
- Short-lived hydrocarbons constrain the gross oxidation during transport. Assuming a 10 hour transit time and an OH distribution peaked at noon, we estimate peak [OH] ≈ $1x10^7$ molecules/cm^3 (0.3 ppt). Similar values have been observed in rural sites in Colorado and Germany.

Ozone Production Photochemistry



Nitrogen Oxide Measurements

NO & NO_y

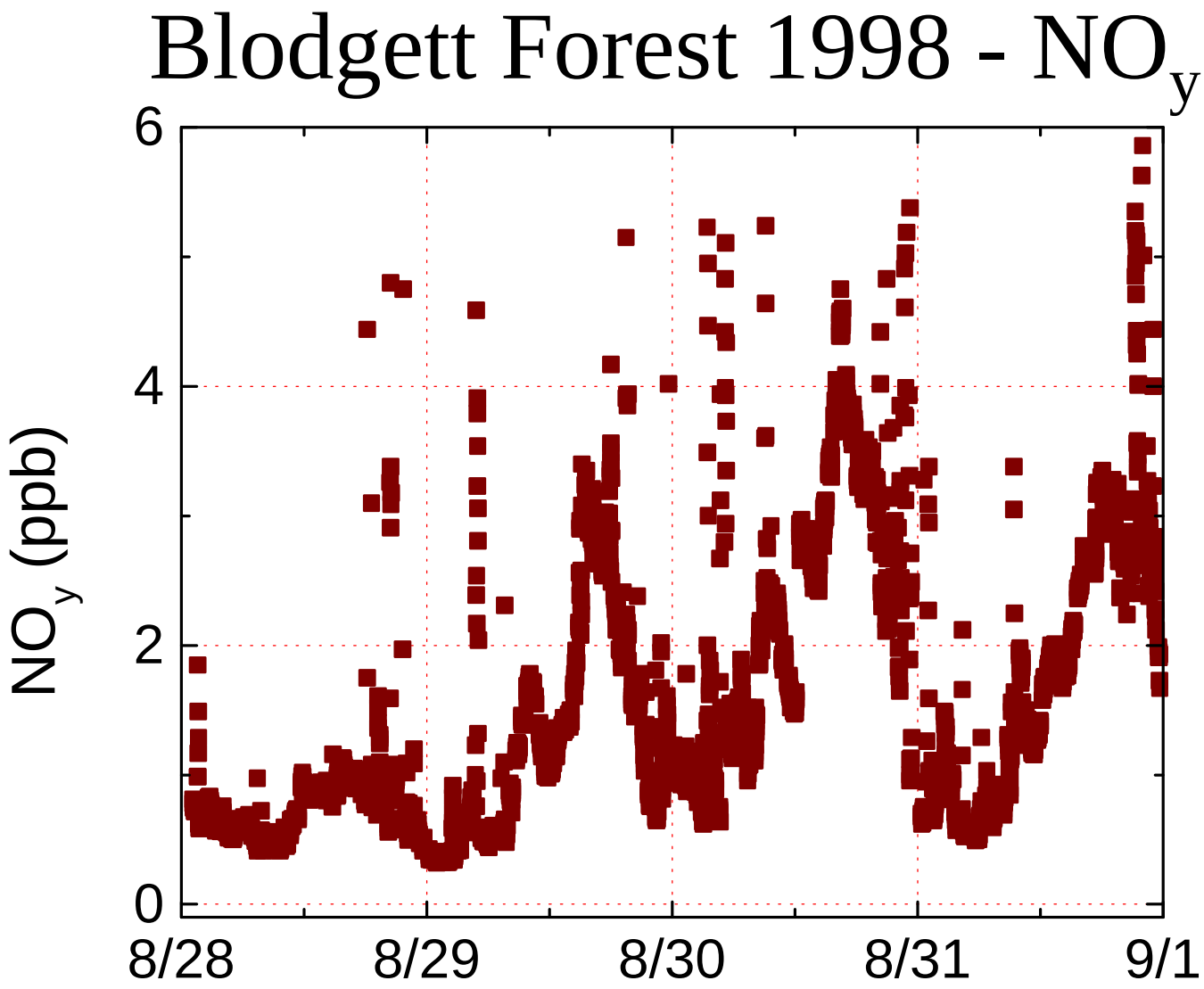
- NO detection with TECO 42CTL

(extra thanks to Ash & CARB for the loan)

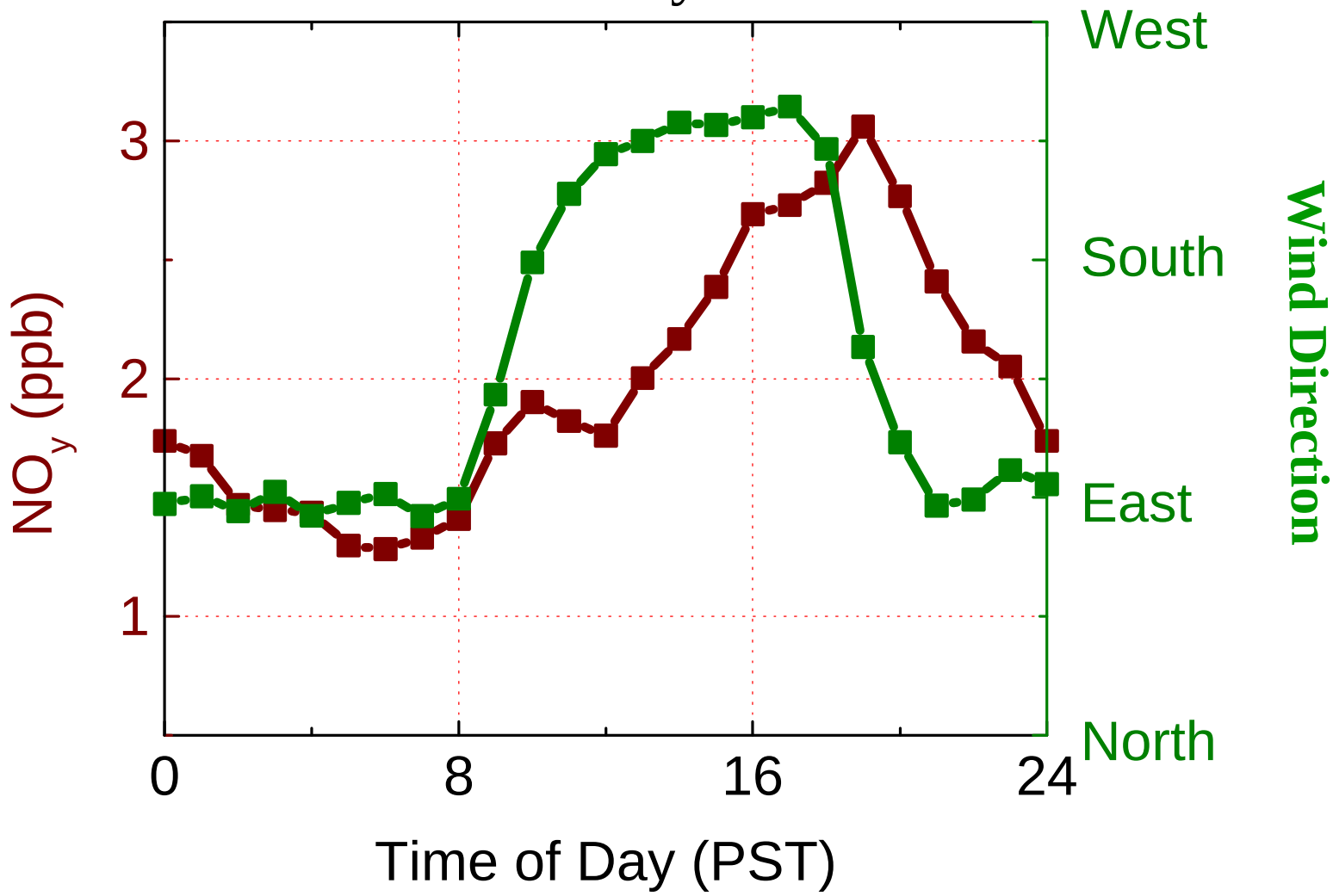
- Accuracy: ± 10%
- Background: ±50 ppt
- NO_y => NO with MO converter (95%)

NO_2

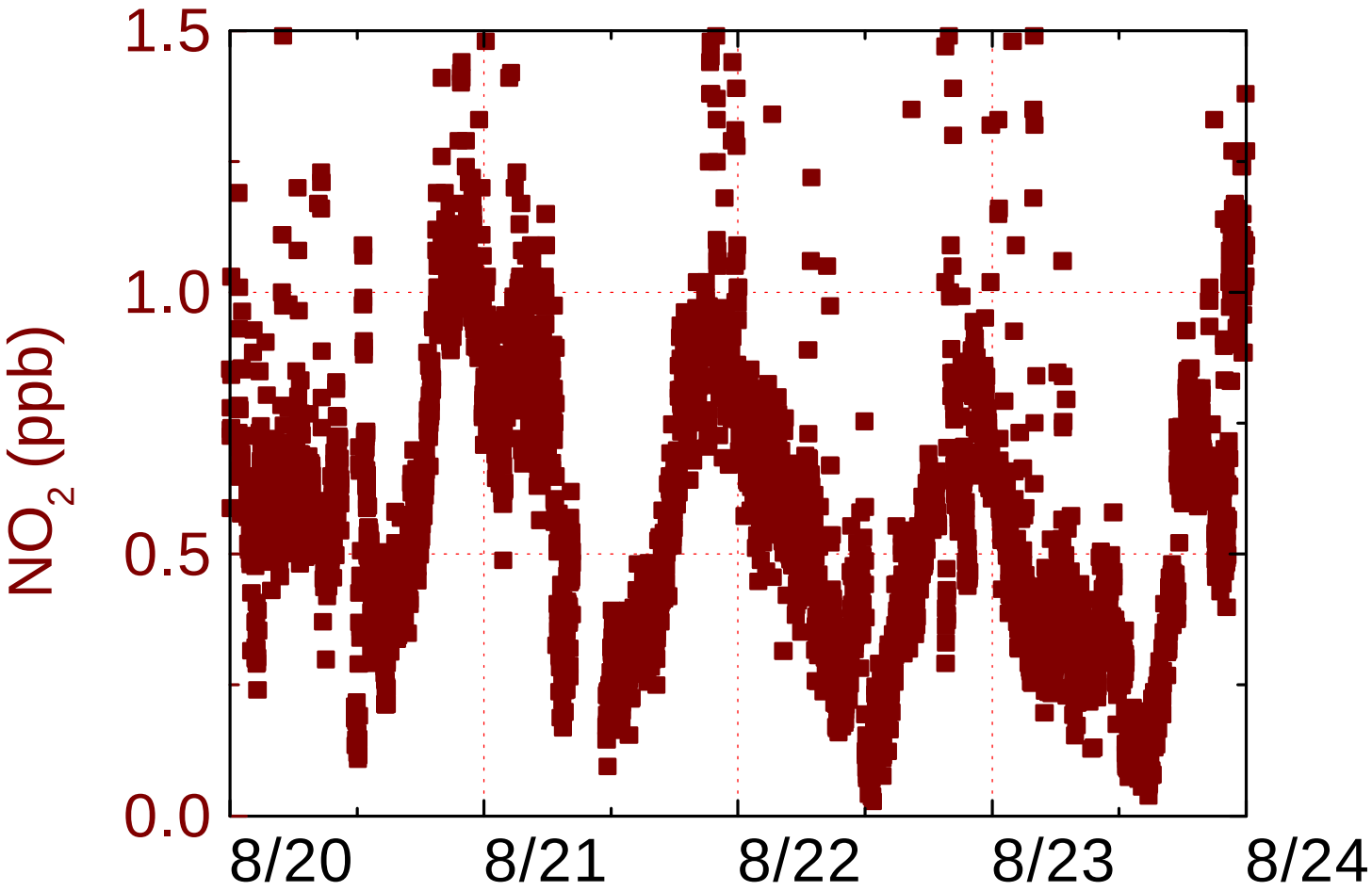
- LIF detection
- Sensitivity: 85 ppt (10sec) -1998
  - current 15ppt (10sec)
- Accuracy: ± 5%


Blodgett Forest 1998 - NOy
NOy (ppb)
6
4
2
0
8/28
8/29
8/30
8/31
9/1

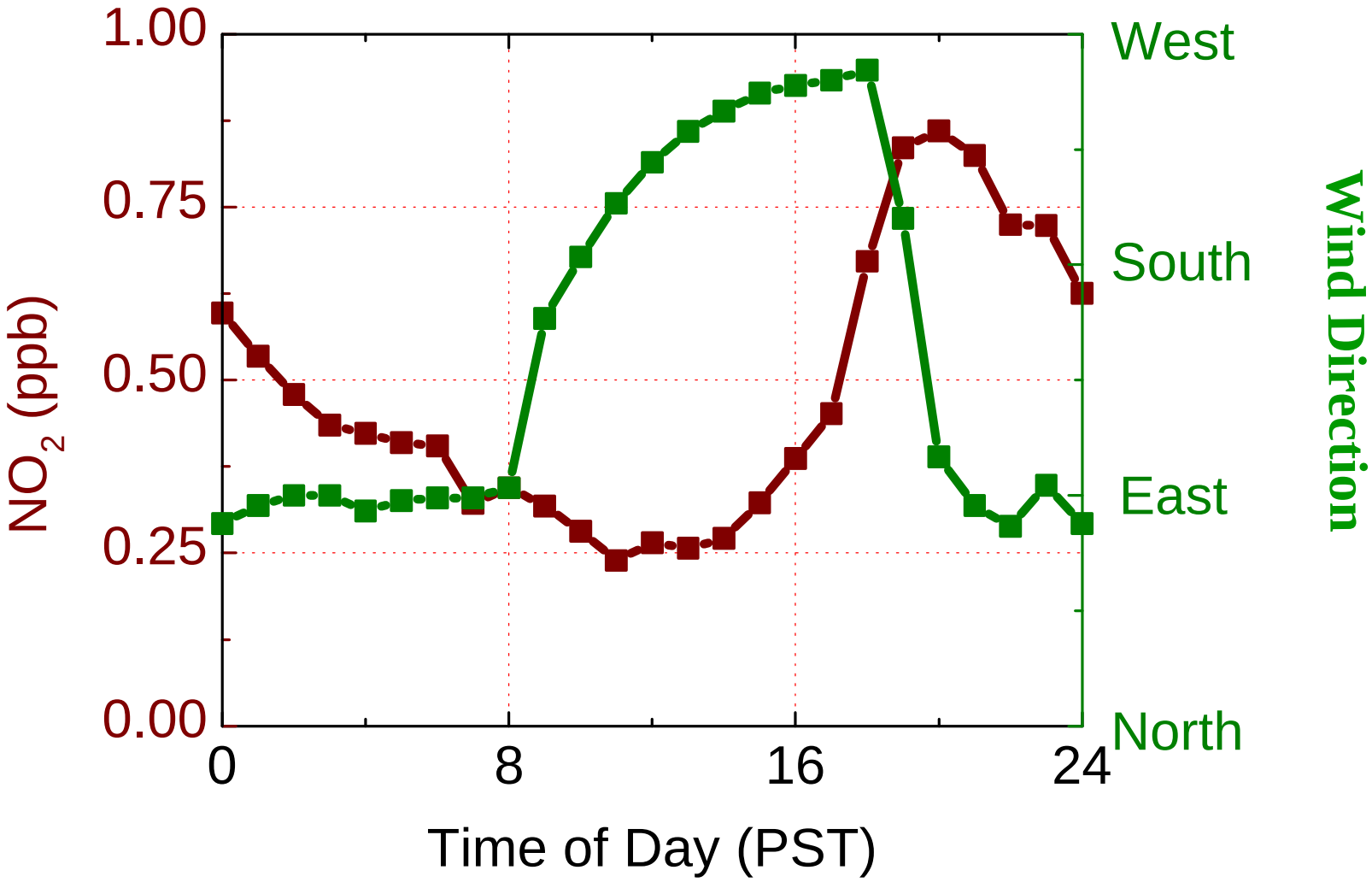
Blodgett Forest NO_y - Diurnal Cycle



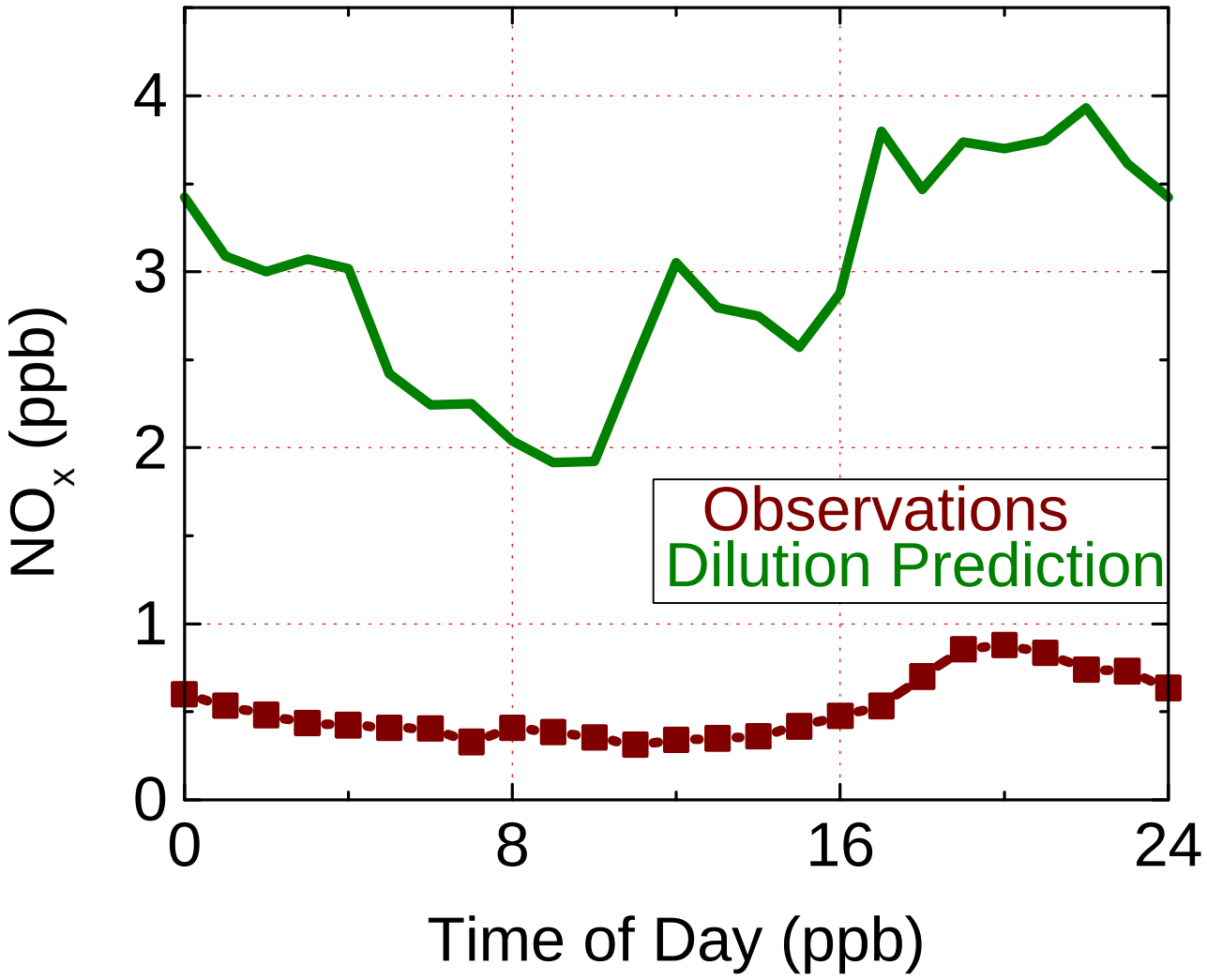
Blodgett Forest 1998 - NO_2



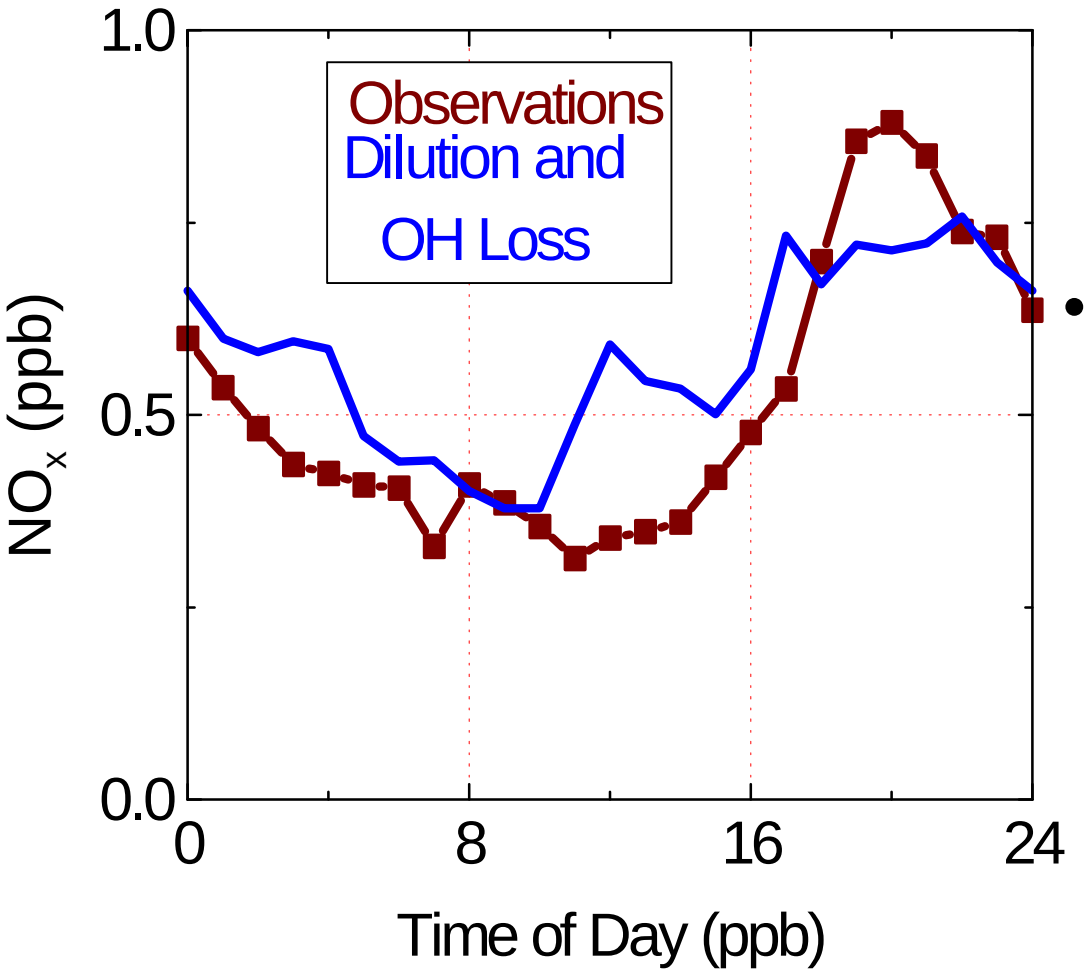
Blodgett Forest NO_2 - Diurnal Cycle



Transport of NO_x

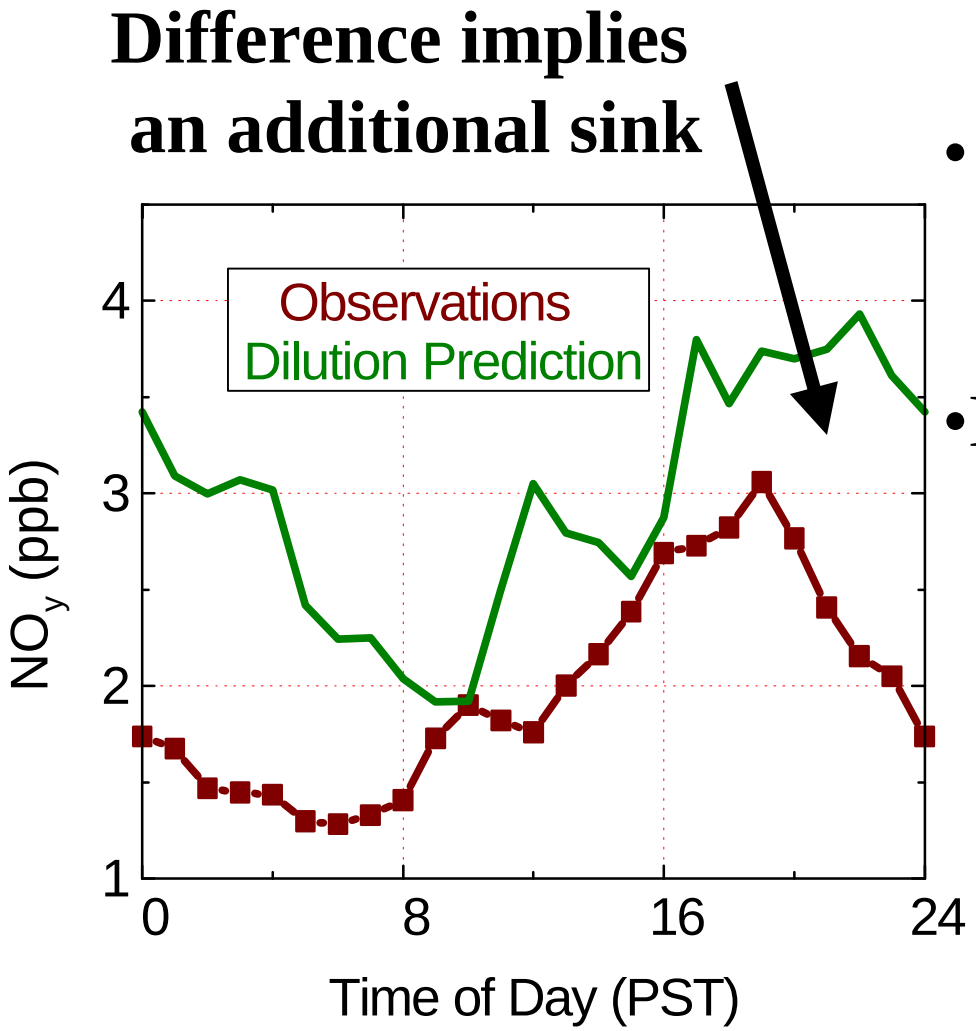


Oxidation of NO_x



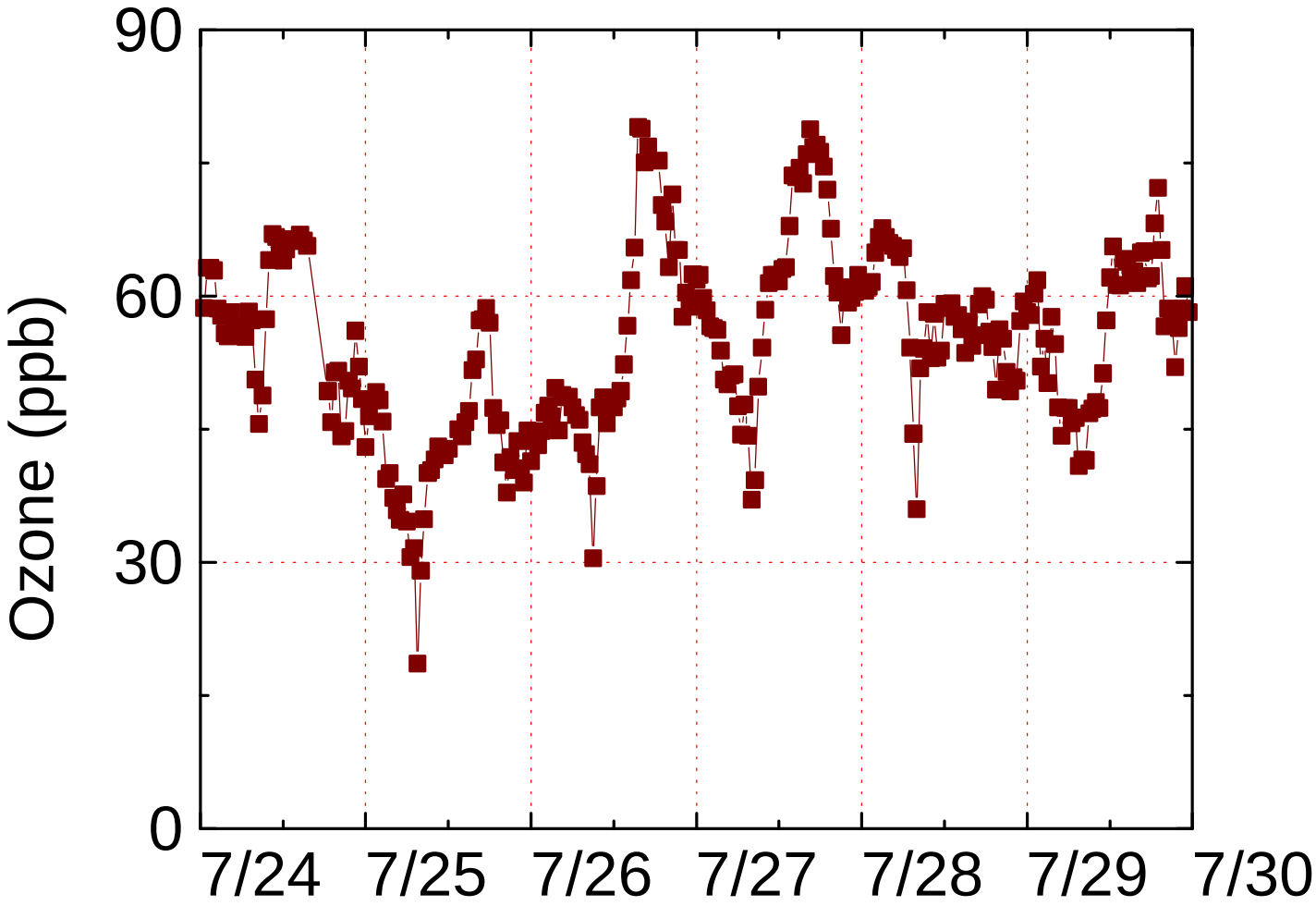
- Mid-day overpredicted
  - NO_x deposition
  - NO_x reactions with RO_2 & RO
- Peak underpredicted
  - NO_x source
  - NO_x reformation most likely from PAN compounds
  - PAN formation competes with $OH+NO_2$

Transport and Oxidation of NO_y

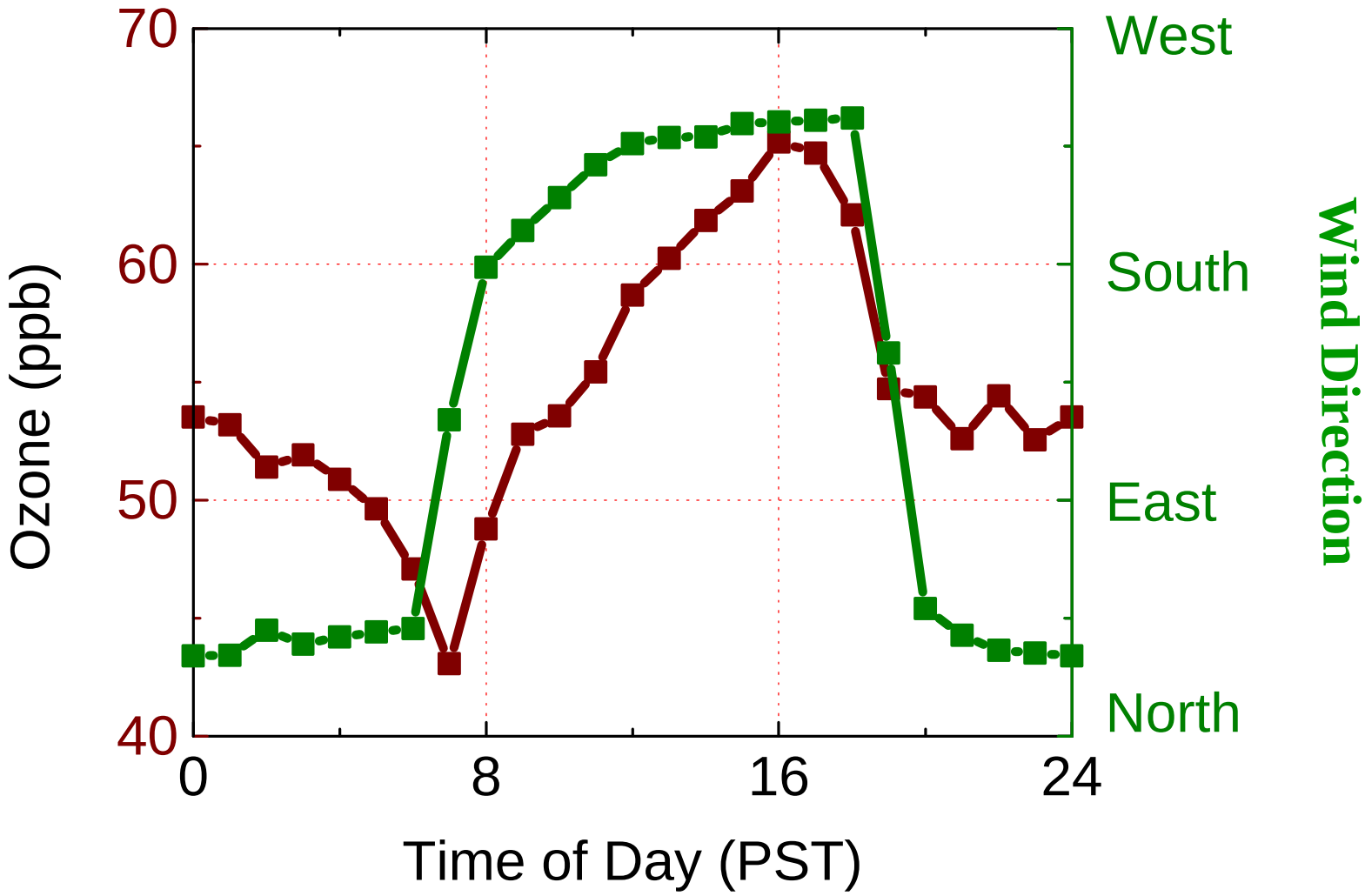


- HNO_3 deposition of V_d = 0.9 cm/s would give good agreement.
- However, deposition rates observed in other studies, 5-7 cm/s, imply only 37% NO_x is converted to HNO_3. This is consistent with other evidence for PAN & biogenic nitrate formation.

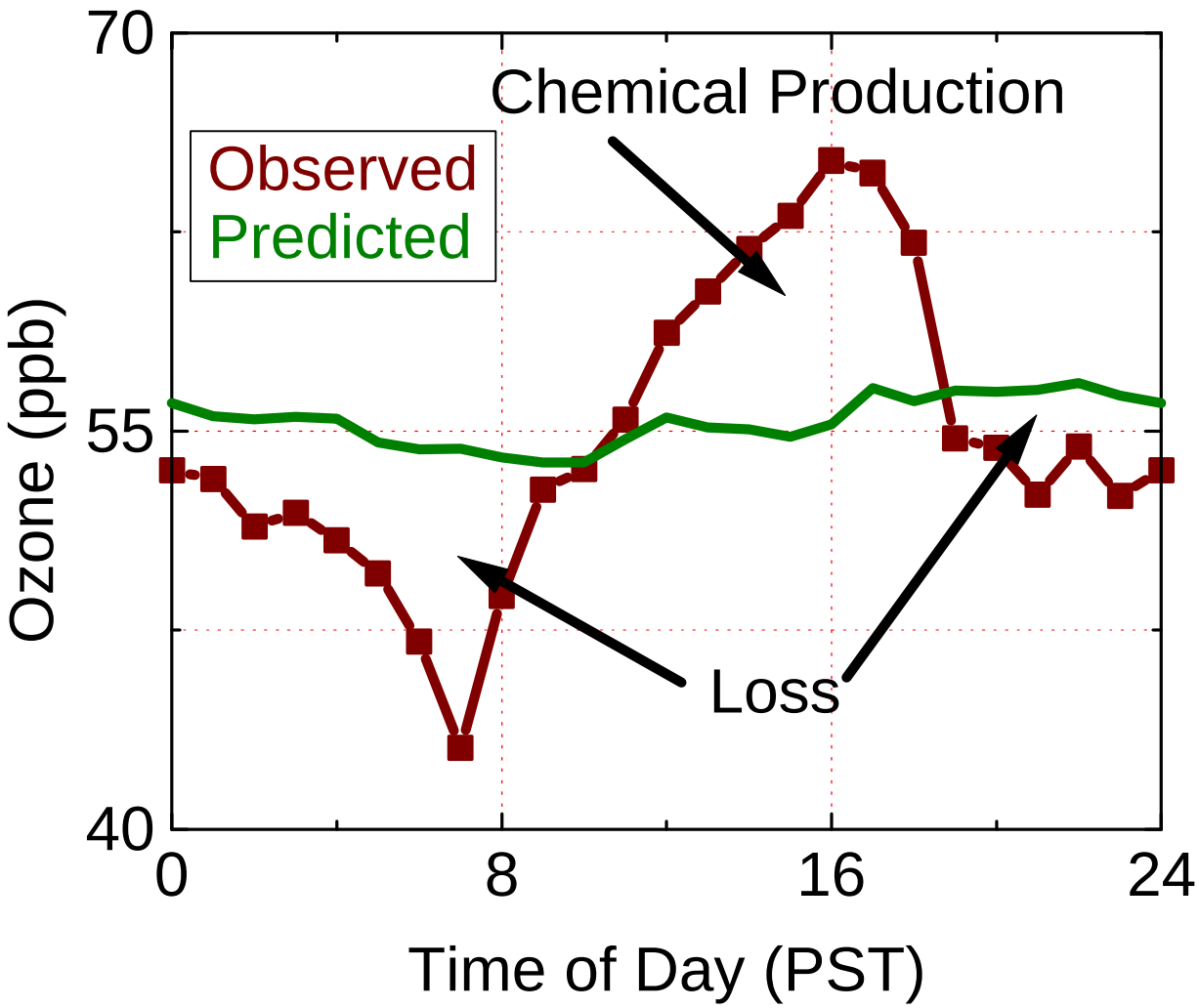
Blodgett Forest 1997 - Ozone

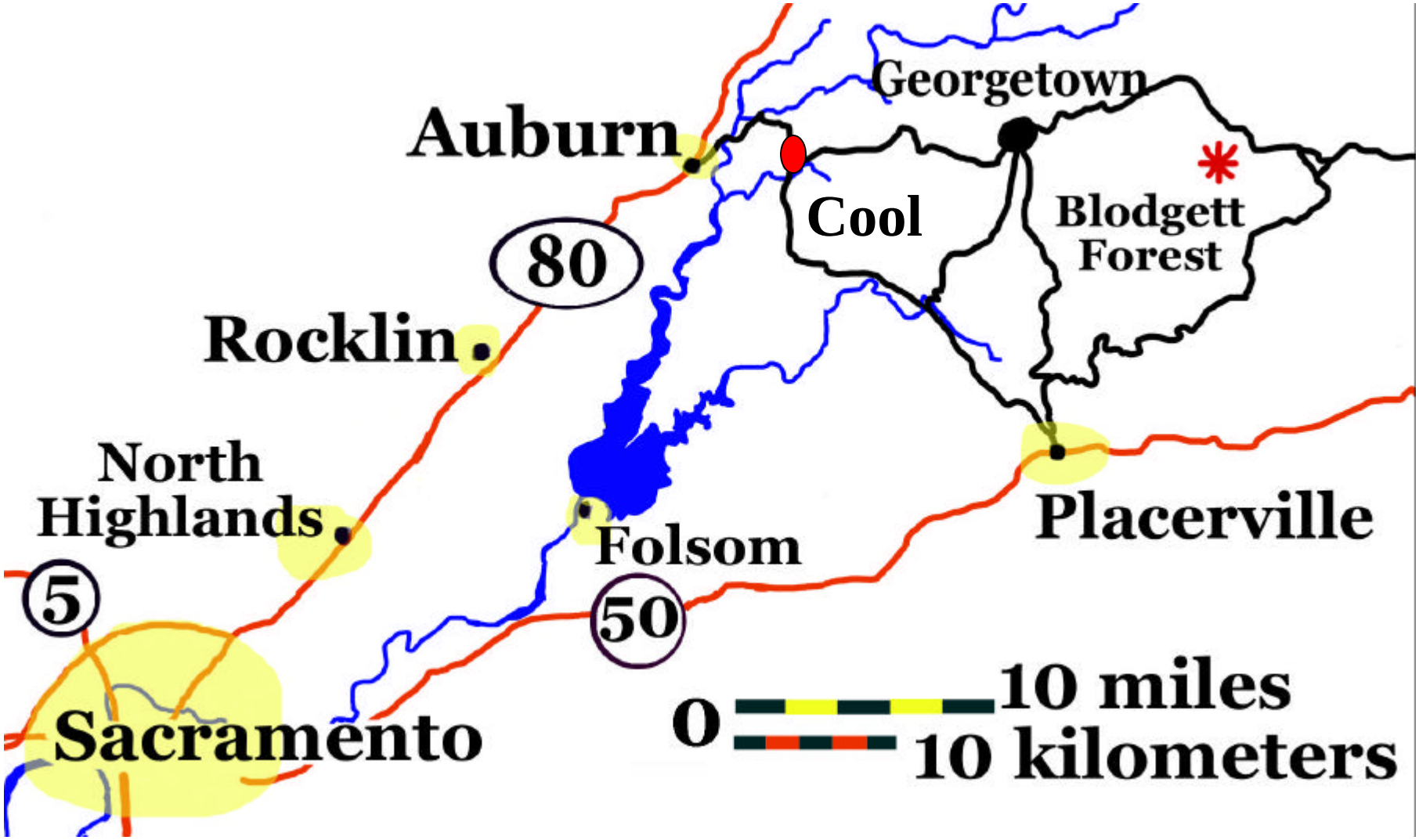


Blodgett Forest O_3 - Diurnal Cycle



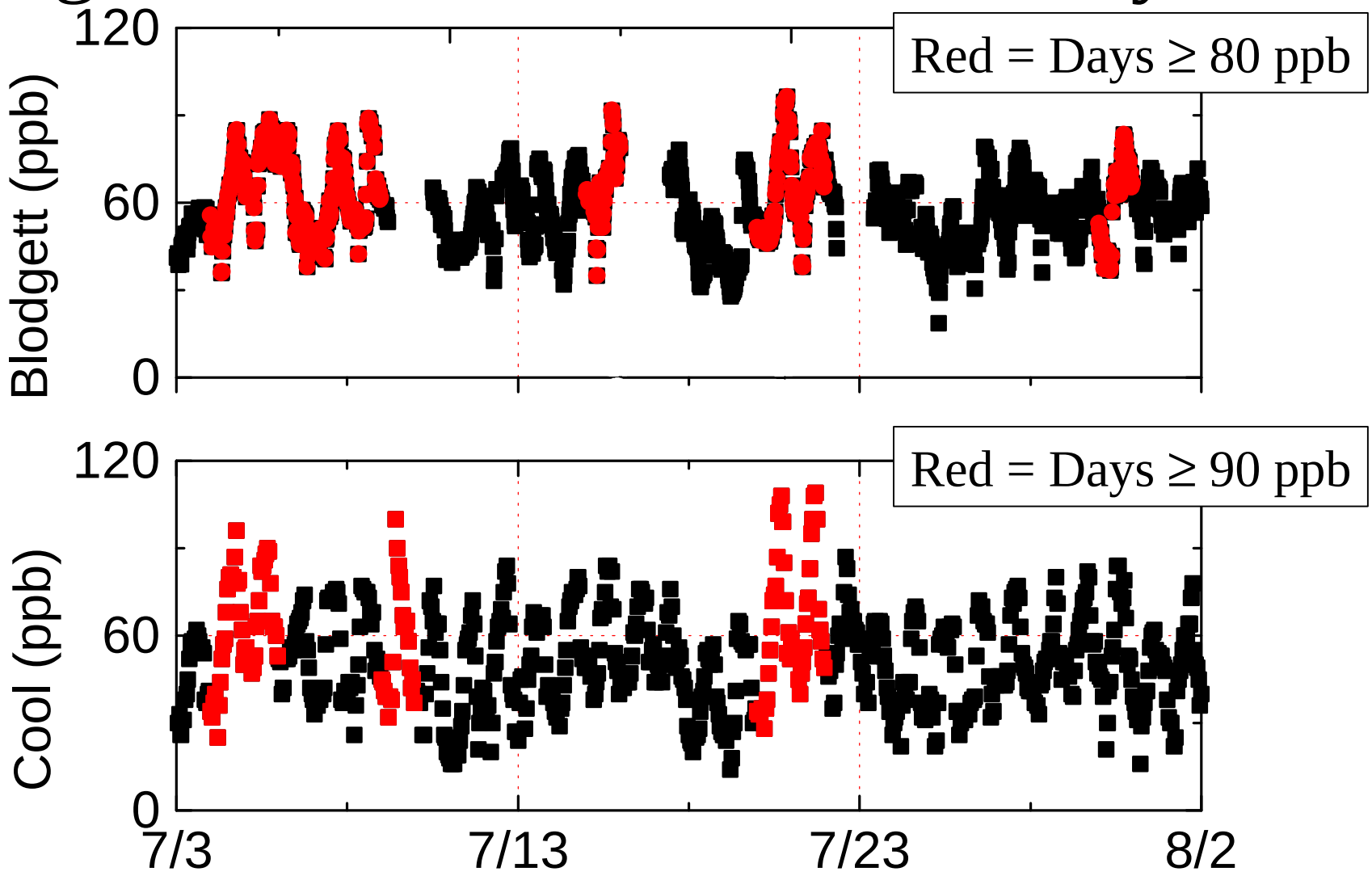
Transport, Deposition, and Chemical Production of Ozone





Drawn from USGS maps

Highest Ozone Observations - July 1997



What Contributes to the High Ozone Events?

- 50% more transport from Sacramento Valley
  - 30% of Sacramento air at Blodgett
    instead of 20%
- No change in the oxidation rate during transport
  - the product of OH & time is constant
- Peak NO_y increases 40%
- Peak NO_x **decreases** 23%
- Temperature increases 2°C

Conclusions:

- Observations of hydrocarbons, meteorology, ozone, NO_x, and NO_y provide insight into and quantitative constraints on :
    - Transport and mixing/diffusion of the urban plume
    - OH abundances
    - NO_y deposition and emission rates
    - Competition between HNO_3 and organic nitrate formation
- The highest ozone is observed when transport of the NO_y rich urban plume penetrates deep into the foothills. These events are also correlated with warmer days (+2°C) when biogenic emissions are highest and PAN reservoirs of NO_x are least stable.
- Future work will focus on understanding the role of biogenically derived nitrates (e.g. isoprene nitrates) on ozone and on measuring NO_y deposition rates.